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(54) [Title of the Invention]

Resin Composition for Encapsulating Semiconductors, and the Semiconductor Device That Uses this Composition.

(57) [Summary]

[Objective]

To offer the semiconductor device that uses the resin composition for encapsulating the semiconductor which has not only safety properties but which also has excellent soldering heat resistance and high temperature reliability.

[Method to Achieve the Objective]

The semiconductor is encapsulated by using the semiconductor- encapsulating- resin

composition that is comprised of the below listed components (2) ~ (9), in which the content of the fire retardant agent (9), of which the main component is the organic fire retardant agent, is 1 ~ 20 wt % of the total of the said resin composition.

(2) Thermosetting resin

(I) Curing agent

(9) Fire retardant agent of which the main component is an organic fire retardant agent.

[Scope of the Patent Application]

[Claim 1]

Semiconductor- encapsulating- resin composition that is comprised of the following components (2) ~ (9).

(2) Thermosetting resin

(I) Curing agent

(9) Fire retardant agent of which the main component is an organic fire retardant agent.

[Claim 2]

Semiconductor- encapsulating- resin composition characterized by the fact that the content of the fire retardant agent (9), of which the main component is the organic fire retardant agent, is 1 ~ 20 wt % of the total of the said resin composition, in the semiconductor encapsulating resin composition described in Claim 1.

[Claim 3]

Semiconductor encapsulating resin composition in which the organic fire retardant agent is a hetero cyclic compound, as was described in Claim 1 or Claim 2.

[Claim 4]

Semiconductor encapsulating resin composition in which the thermal degradation initiation temperature of the organic fire retardant agent is 260 °C or higher, as was described in any one of Claims 1 to 3.

[Claim 5]

Semiconductor encapsulating resin composition in which the content of chlorine ions in the cured body is 200 μg or less per 1 g of cured body, as was described in any one of Claims 1 to 4.

[Claim 6]

Semiconductor encapsulating resin composition in which the cured body of the semiconductor encapsulating resin composition shows the fire retardant ability equivalent to V-0 in the UL burning test with a thickness of 1/16 inch, as was described in any one of Claims 1 to 5.

[Claim 7]

Semiconductor device made by encapsulating the semiconductor using the semiconductor encapsulating resin composition described in any one of Claims 1 to 6.

[Detailed Explanation of the Invention]

[0001]

[Technical Field in Which this Invention Belongs]

This invention relates to the semiconductor encapsulating epoxy resin composition with excellent fire retarding ability, excellent solder heat resistance and excellent high temperature reliability, and also the semiconductor device that uses this resin.

[0002]

[Existing Technology]

Semiconductor elements such as transistors, ICs, LSIs, etc., used to be encapsulated by ceramic and they used to be made into semiconductor devices, however, recently, from the view point of the cost and the mass production ability, resin encapsulation that uses epoxy resin is becoming mainstream. By the way, the electronic parts such as the semiconductor devices, etc., must meet the UL 94 V-0 standard for fire retardation. Until now, as the method to add the fire retardant ability to the semiconductor encapsulating

epoxy resin composition, brominated epoxy resins and antimony oxide have been added generally, but the semiconductor devices that use this method have the following problems. Toxic gases such as hydrogen bromide, bromine, brominated antimony, etc., are generated during the burning time, and in addition, when it is left for a long time at high temperature, the aluminum wiring of the semiconductor element can be corroded by the free bromine that is generated, and the degree of high reliability decreases. Also, the method to use a metal hydroxide as the fire retardant agent has been suggested, but the semiconductors that use this method have the following problems too. The first problem is a decrease in the soldering heat resistance when surface-mounting the semiconductor. Namely, when the semiconductor device is exposed to high temperature (normally 215 ~ 260 °C) due to the treatment of submersion soldering, infrared reflow, vapor phase reflow, etc., the water that was retained in the metal hydroxide is suddenly vaporized, and by this, the semiconductor device experiences expansion or cracking, therefore, the soldering heat resistance decreases. The second problem is that the semiconductor element function in a high temperature environment of 150 ~ 200 °C decreases, namely the high temperature reliability decreases. Namely, in the semiconductor element with large heat generation or in the semiconductor device that is used in a high temperature environment, the de-watering reaction of the metal hydroxide occurs as a result of long time use, and the high temperature reliability decreases.

[0003]

Therefore, in order to solve the problems like these, the applicant of this invention had suggested the semiconductor encapsulating thermosetting resin composition that use both metal hydroxide and metal oxide as the fire retardant agent, and they have improved the safety, the soldering heat resistance and the high temperature reliability of the resin-encapsulated semiconductor device by using the said resin composition. (A Tokuhyo@ H7-806085 Official Gazette)

[0004]**[Problem That this Invention Intends to Solve]**

However, accompanying the recent development of technology in the semiconductor

field, even better soldering heat resistance and high temperature reliability have been desired, and even the semiconductor encapsulating thermosetting resin composition that uses the fire retardant agent that co-uses both the above mentioned metal hydroxide and metal oxide, is not sufficiently reliable for some semiconductor elements. Also, in the case when a metal hydroxide is used as the fire retardant agent, or in the case when a metal hydroxide and a metal oxide are used, the flow ability of the semiconductor encapsulating resin composition during the forming time decreases, and depending on the shape of the semiconductor package, the forming becomes impossible. This invention was made based on this situation, and the objective is to offer the semiconductor encapsulating resin composition with excellent fire retardant ability, excellent soldering heat resistance, excellent high temperature reliability, excellent forming ability and safety, and also the semiconductor device that uses this.

[0005]**[Method to Solve the Problem]**

The inventors investigated and discovered that if an organic fire retardant agent is used as the main component of the fire retardant agent, not only can solder heat resistance and high temperature reliability be obtained, but also the good forming ability can be obtained, and this invention was made.

[0006]

Namely, this invention is the semiconductor- encapsulating- resin composition that is comprised of the following components (2) ~ (9).

(2) Thermosetting resin

(1) Curing agent

(9) Fire retardant agent of which the main component is an organic fire retardant agent.

[0007]

Also, this invention is the semiconductor device which is made by encapsulating the semiconductor element using the above mentioned semiconductor encapsulating resin composition.

[0008]

[Form of Bringing this Invention into Practice]

Next, the form to bringing this invention into practice will be explained in detail.

[0009]

The semiconductor encapsulating resin composition of this invention can be obtained from the thermosetting resin (component 2), the curing agent (component []) and the fire retardant agent (component 9) of which the main component is an organic fire retardant agent, and normally, it is in the form of a powder or a tablet.

[0010]

As the above mentioned thermosetting resin (component 2), epoxy resin, poly maleimide resin, unsaturated polyester resin, phenolic resin, etc., can be listed. Especially, in this invention the use of epoxy resin and poly maleimide resin is preferred.

[0011]

The above mentioned epoxy resin is not particularly limited, and the already known ones can be used. For instance, the bisphenol A type, the phenolic novolac type, the cresol novolac type, the biphenyl type, the phenylene type, etc., can be listed.

[0012]

The above mentioned poly maleimide resin is not particularly limited, and already known ones that have 2 or more maleimide groups in their molecule can be used. For instance, N, N=-4, 4'- di-phenyl methane bis maleimide; 2, 2-bis-[4-(maleimide phenoxy) phenyl] propane, etc., can be listed.

[0013]

As the curing agent (component []) that is used with the above mentioned thermosetting resin (component 2), the already known ones, for instance the phenolic resins, acid anhydrides, amine compounds, etc., can be used. In the case when an epoxy resin is

used as the above mentioned thermosetting resin, a phenolic resin should be used suitably. Phenolic novolac resin, cresol novolac resin, bisphenol A type novolac resin, naphthol novolac resin and phenol aralkyl resin, etc., can be listed as the above mentioned phenolic resins.

[0014]

Also, the curing agent when poly maleimide is used as the thermosetting resin is not particularly limited and the already known ones can be used. For instance, the alkenyl phenols which can be obtained by reacting the above mentioned epoxy resin curing agent in the presence of an allyl halide and an alkali, or amines can be listed.

[0015]

In the case when the above mentioned thermosetting resin (component 2) is epoxy resin, and the above mentioned curing agent (component []) is phenolic resin, the content proportions of these should be set preferably in the way that the hydroxyl group content of the phenolic resin becomes 0.7 ~ 1.3 equivalents for 1 equivalent of the epoxy groups in the above mentioned epoxy resin, and more preferably it should be set to equal 0.9 ~ 1.1 equivalents.

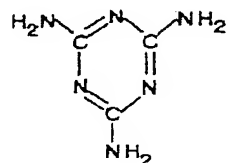
[0016]

In this invention, the fire retardant agent of which the main component is an organic fire retardant agent is used with the thermosetting resin (component 2) and the curing agent (component []). Here, in this invention, the fire retardant agent of which the main component is an organic fire retardant agent, includes the ones which are comprised of only a organic fire retardant agent too. The content of the organic fire retardant agent in the fire retardant agent should be preferably 95 ~ 100 wt %. Hetero cyclic compounds, nitrogen- containing compounds, phosphorus- containing compounds, etc., can be listed as the organic fire retardant agents, and the hetero cyclic compounds are especially preferred for use. Concerning the hetero cyclic compound, for instance the hetero cyclic compounds that have a tri azine ring such as melamine (shown by Chemical Formula 1) or cyanuric acid (shown by Chemical Formula 2), the derivatives of cyanuric acid such as

iso cyanuric acid (shown by Chemical Formula 3) or melamine cyanurate (shown by Chemical Formula 4), etc., and the compounds that have a phosphazene ring (shown by, for instance Chemical Formula 5), etc., can be listed. These can be used alone or in combinations of 2 or more.

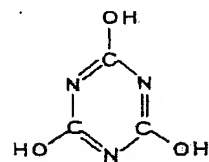
[0017]

[Chemical Formula 1]



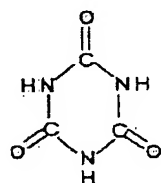
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[Chemical Formula 2]



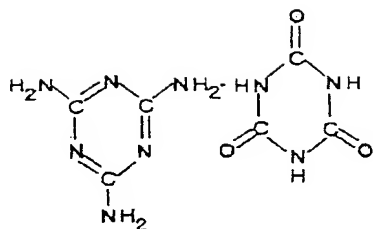
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[Chemical Formula 3]



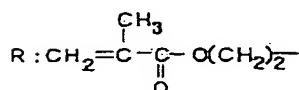
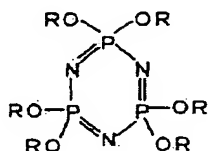
[0020]

[Chemical Formula 4]



[0021]

[Chemical Formula 5]



[0022]

Concerning fire retardant agents other than organic ones, inorganic fire retardant agents such as metal oxides, metal hydroxides, etc., can be used at 0 ~ 5 wt % of the fire retardant agent.

[0023]

The content of the fire retardant agent of which the main component is organic, should be 1 ~ 20 wt %, preferably 5 ~ 15 wt %, more preferably it should be in the range of 9 ~ 15 %, of the total semiconductor encapsulating resin composition. If this content is too low, the fire retardant effect is poor. On the other hand, if the content is too high, the high temperature reliability and the solder heat resistance tend to decrease.

[0024]

The temperature at which the thermal degradation of the above mentioned organic fire retardant agent begins should be preferably 260 °C or higher (normally, the upper limit is 500 °C). If the thermal degradation initiation temperature is less than 260 °C, thermal

degradation starts sooner than the thermal degradation of the organic components other than the organic fire retardant agent that are included in the semiconductor encapsulating resin composition of this invention, therefore the fire retardant ability decreases. Here, the thermal degradation initiation temperature of the organic fire retardant agent is the value that is measured by thermogravimetric analysis that uses a thermobalance with a temperature increase rate of $10^{\circ}\text{C} / \text{min}$, and it is whichever is the lower temperature of the temperature at which the weight loss reaches 5 wt %, and the temperature at which the differential weight loss value (the value where weight loss is first order differentiated in time, namely the rate of weight loss) exceeds 0.5 wt %.

[0025]

Concerning the semiconductor encapsulating resin composition that includes the fire retardant agent of which the main component is the above mentioned organic fire retardant agent, preferably the chlorine ion content that is extracted in the following manner should be $200\ \mu\text{g}$ or less for 1 g of the cured body of the above mentioned resin composition. Namely, 5 g of the cured body of the resin composition and 50 cc of distilled water are put into a simple autoclave, and this autoclave is left in a drying oven at 160°C for 20 hours, and the extraction water is obtained (the pH should be in the range of 6.0 ~ 8.0). This extraction water is analyzed by ion chromatography, and the amount of chlorine ions (X) is measured. This chlorine ion content (X) is the value where the ions in the cured body of the resin composition are diluted 10 times, therefore, the chlorine ion content per 1 g of the resin composition cured body is calculated by the following equation.

[0026]

Chlorine ion content (μg) per 1 g of the resin composition cured body = $X \times (50/5)$

[0027]

Namely, if the chlorine ion content included in 1 g of the resin composition cured body is higher than $200\ \mu\text{g}$, corrosion of the semiconductor element or leads might occur, and the moisture resistance reliability tends to decrease.

[0028]

In order to make the chlorine ion content included in 1 g of the resin composition cured body to be less than 200 μg , the chlorine ions in the above mentioned organic fire retardant agent should be preferably 50 ppm per 1 g. Here, the chlorine ion content in the organic fire retardant agent can be obtained by replacing the resin composition cured body with the organic fire retardant agent, in the above mentioned method for measuring the chlorine ion content in the cured body of the resin composition.

[0029]

The semiconductor encapsulating thermosetting resin composition of this invention can include an inorganic filler, a curing promotion agent, pigments, a mold separating agent, a flexibility adding agent, etc., in addition to the above mentioned (2) ~ (9), depending on necessity.

[0030]

Quartz glass powder, talc, silica powder, alumina powder, calcium carbonate, etc., can be listed as the inorganic fillers. Especially, the use of silica powder is suitable.

Concerning the content of the inorganic fillers, in the case of silica powder, it is preferred to make the total amount of the inorganic filler, inorganic fire retardant agent and the organic fire retardant agent to be 60 wt % or greater of the entire resin composition. More preferably it should be 70 wt % or greater (normally the upper limit is 93 wt %). Namely, if the content of total inorganic material is less than 60 wt %, the fire retardant ability tends to decrease.

[0031]

Concerning the above mentioned curing promotion agent, the already known materials, for instance, 1, 8-di-aza-bicyclo (5, 4, 0) undecene-7; tertiary amines such as tri ethylene diamine, etc.; imidazoles such as 2- methyl imidazole, etc.; phosphorus type curing promotion agents such as the tri phenyl phosphine, tetra phenyl phosphonium tetra phenyl borate, etc., can be listed.

[0032]

Carbon black, titanium oxide, etc., can be listed as the above mentioned pigment.

[0033]

Concerning the mold separation agent, poly ethylene wax, paraffins, or fatty acid esters, fatty acid salts, etc., can be listed.

[0034]

Concerning the flexibility adding agent, coupling agents such as silane coupling agents, etc., silicone resins, and the butadiene - acrylonitrile rubber, etc., can be listed.

[0035]

The semiconductor encapsulating resin composition of this invention can be produced for example, as follows. Namely, the thermosetting resin (component 2), the curing agent (component []) and the fire retardant agent (component 9) of which the main component is an organic fire retardant agent, and other additives if necessary, are blended in the prescribed proportions. Then, this mixture is melt-kneaded with heating by using a kneader such as a mixing roll machine, etc., and then it is cooled to room temperature. Then this is crushed by an already known method, and if necessary, it is made into tablets. By this series of processes, the objective resin composition can be produced. The method for encapsulating the semiconductor element is not particularly limited, and it can be done by an already known method such as ordinary transfer forming, etc.

[0036]

Next, Actual Examples and Comparisons will be explained.

[0037]

[Examples 1 ~ 9, and Comparisons 1 ~ 3]

Each of the components shown in Tables 1 and 2 was blended in the proportions listed,

and it was melt- kneaded for 3 minutes with a mixing roll (100 °C), and after it was cooled down, it was crushed, and the thermosetting resin composition was obtained in powder form. Among the above mentioned components, the thermal degradation initiation temperature of the melamine, cyanuric acid and melamine cyanurate that were used as the organic fire retardant agent were 270 °C, 310 °C and 320 °C, respectively. Using the thermosetting resin compositions obtained in the Examples and Comparisons, the semiconductor element was transfer- formed (conditions : 175 °C x 2 minutes), and it was post-cured at 175 °C x 5 hours, and thus, the semiconductor device was obtained. This semiconductor device was an 80 pin QFP (quad flat pack, size : 20 x 14 x 2 mm), and the "di pad" (*phonetically written*) size was 8 x 8 mm. The semiconductor device obtained like this was left in a high temperature tank at 85 °C / 85 % relative humidity for 96 hours to absorb the moisture, and thereafter, it was infrared reflowed for 90 seconds at a heating temperature of 240 °C, and the soldering heat resistance was evaluated. Also, the above mentioned semiconductor device was left at 200 °C, and the time at which the failure rate became 50 % was measured, and this was used for the evaluation of the high temperature reliability. In addition, the test specimen with a thickness of 1/16 inch was formed, and the fire retardant ability was evaluated according to the UL 94 V-0 standard. Also, the resin composition cured body was crushed, and using this as the sample, the thermal degradation initiation temperature of the resin composition cured body was measured by the above mentioned method. Also, the content of chlorine ions per 1 g of cured body of the resin composition was measured according to the above mentioned method. Also, the spiral flow value and the flow tester viscosity were measured as the indicators of the forming ability of the resin composition. These results are shown in Table 3 and Table 4.

[0038]

[Table 1]

		Actual Example								
		1	2	3	4	5	6	7	8	9
Epoxy resin (weight parts)	Cresol novolac type	63.8			63.8	63.8		63.8	63.8	63.8
	Biphenyl type		51.8	51.8			51.8			
Phenolic resin (weight parts)	Novolac type	34.2			34.2	34.2		34.2	34.2	34.2
	Aralkyl type		46.2	46.2			46.2			
Organic fire retardant agent (weight parts)	Melamine	50			70					
	Cyanuric acid		50			70				
	Melamine cyanurate			80			100	70	50	120
Inorganic fire retardant agent (weight parts)	Mg (OH) ₂				3	2	1	0.5		
	NiO					1	0.5	0.5		
Silica (weight parts)		199	349	559	339	455	499	799	799	399
Phosphorus type curing promoting agent (weight parts)		1	1	1	1	1	1	1	1	1
Ester type wax (weight parts)		0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Olefin type wax (weight parts)		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Carbon black (weight parts)		1	1	1	1	1	1	1	1	1
Total (weight parts)		350	500	740	513	629	701.5	971	950	620
Content of organic fire retardant agent in fire retardant agent (wt %)		100.00	100.00	100.00	95.89	95.89	98.52	98.59	100.00	100.00
Content of fire retardant agent in the entire resin composition (wt %)		14.3	10.0	10.8	14.2	11.6	14.5	7.3	5.3	19.4
Total content of fire retardant agent and inorganic filler in entire resin composition (wt %)		71.1	79.8	86.4	80.3	83.9	85.6	89.6	89.4	83.7

[0039]

[Table 2]

		Comparisons		
		1	2	3
Epoxy resin (weight parts)	Cresol novolac type		63.8	63.8
	Biphenyl type	51.8		
Phenolic resin (weight parts)	Novolac type		34.2	34.2
	Aralkyl type	46.2		
Organic fire retardant agent (weight parts)	Melamine			
	Cyanuric acid	200		
	Melamine cyanurate		2	
Inorganic fire retardant agent (weight parts)	Mg (OH) ₂			50
	NiO			
Silica (weight parts)		459	409	349
Phosphorus type curing promoting agent (weight parts)		1	1	1
Ester type wax (weight parts)		0.2	0.2	0.2
Olefin type wax (weight parts)		0.8	0.8	0.8
Carbon black (weight parts)		1	1	1
Total (weight parts)		760	512	500
Content of organic fire retardant agent in fire retardant agent (wt %)		100.00	100.00	0.00
Content of fire retardant agent in the entire resin composition (wt %)		26.3	0.4	10.0
Total content of fire retardant agent and inorganic filler in entire resin composition (wt %)		86.7	80.3	79.8

[0040]

[Table 3]

	Actual Example								
	1	2	3	4	5	6	7	8	9
Solder heat resistance (Crack occurring ratio in the Infrared reflow test) (pieces / 10 pieces)	0/10	0/10	0/10	0/10	0/10	0/10	0/10	0/10	0/10
High temperature reliability (50 % failure occurring time at 200 °C) (h)	700	700	800	800	700	700	700	700	700
Fire retardant ability (UL94 V-0)	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Thermal degradation starting temperature of cured body of resin composition (°C)	300	290	290	300	300	290	300	300	300
Chlorine ion (μg) in 1 g of cured body of resin composition	40	10	35	40	15	45	30	20	30
Spiral flow value (cm)	95	90	100	90	100	80	80	90	80
Flow tester viscosity (poise)	100	90	110	250	200	200	250	150	230

[0041]

[Table 4]

	Comparison		
	1	2	3
Solder heat resistance (Crack occurrence ratio in the Infrared reflow test) (pieces / 10 pieces)	5/10	0/10	2/10
High temperature reliability (50 % failure occurring time at 200 °C) (h)	300	500	500
Fire retardant ability (UL94 V-0)	Pass	Fail	Fail
Thermal degradation starting temperature of cured body of resin composition (°C)	300	290	300
Chlorine ion (μg) in 1 g of cured body of resin composition	20	10	150
Spiral flow value (cm)	90	100	60
Flow tester viscosity (poise)	90	110	300

[0042]

[Effect of the Invention]

As was described above, in the semiconductor device of this invention, the semiconductor element is encapsulated by using the resin composition that contains the fire retardant agent of which the main component is an organic fire retardant agent. Therefore, compared with the case when a metal hydroxide is used as the fire retardant agent, or the case when a metal hydroxide and a metal oxide are co-used, the effect of water is extremely small, therefore, the solder heat resistance and the high temperature reliability improve, and it exhibits a long life. In addition, the fire retardant agent of which

the main component is an organic fire retardant agent, does not decrease the flow ability of the semiconductor encapsulating resin composition compared with metal hydroxides and metal oxides, therefore, the semiconductor encapsulating resin composition of this invention can exhibit good forming ability for any shape of semiconductor package. In addition, the semiconductor resin composition of this invention and the semiconductor device that uses this, have fire retardant ability without using a toxic halogen compound or antimony trioxide, therefore, it is extremely safe and environmentally friendly.

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